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INSECTICIDE RESIDUES ON AND IN TOMATOES

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In growing tomatoes, insecticides may be required from before planting the seed to within a few days of harvesting the mature tomatoes. During the growing period, protection of the plant and fruit often is necessary to insure a healthy plant with marketable fruit. As harvest approaches, insecticides may be required to insure quality fruit free from unsightly scars from insect feeding, and to insure a market product free of contamination with insect fragments.

Between 1956 and 1962 the Analytical Investigations Laboratory of the Pesticide Chemicals Research Branch, Yakima, Wash., cooperated with the Fruit and Vegetable Insects Research Branch of the Entomology Research Division in a study of insecticide residues on and in tomatoes. Insecticides were applied to the seed, seedbed, or foliage as pellets, granules, dusts, sprays, or baits. The selection and application of insecticides were under the direction of cooperating entomologists.1/ These entomologists collected, quick-froze, and shipped tomato samples by air express to the laboratory. This report covers the analysis of approximately 300 samples of tomatoes examined during this study.

The prime factors in evaluating an insecticide for use on a food or forage crop include (1) effectiveness, (2) phytotoxicity, and (3) amount of residue remaining on the crop at harvesttime.

During this investigation, two chlorinated hydrocarbon and nine organic phosphorus insecticides were field tested and their residues on tomatoes determined. These materials and the residue tolerances established for them by the Food and Drug Administration are as follows:

1/ Howard E. Dorst, Logan, Utah, Kenneth E. Gibson, Twin Falls, Idaho, and Joseph Wilcox, Riverside, Calif.

Insecticide	Established tolerance (p.p.m.)
Aldrin	0.1
Diazinon	0.75
Dimethoate	None
Di-Syston® 1/ (O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate)	0.75
Guthion® (O,O-dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl) phosphorodithioate	2
Heptachlor	0
Malathion	8
Mevinphos (Phosdrin®)	0.25
Naled (Dibrom®)	None
Phorate	None
Trichlorfon (Dylox®)	None

1/ Mention of a proprietary product in this publication does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval by the Department to the exclusion of other products that may also be suitable.

GROWING, SAMPLING, AND SAMPLE PREPARATION

The experimental plots had rows of varying length and were from four to six rows wide. The plots were replicated from two to six times.

Residue samples, either green or green-ripe, were taken from the two center rows of each plot by picking fruit at random in three to five locations per replicate.

The tomatoes either were submitted whole or were quartered and the opposite quarters combined. Samples consisted of opposite quarters from 6 to 12 tomatoes. A few of them were washed before quartering. The residue samples were quick-frozen and shipped in dry ice to the laboratory, where they were stored and kept frozen until prepared for analysis.

LABORATORY PROCEDURES

Aldrin, Heptachlor, and Malathion

The frozen tomatoes were chopped in a mechanical food chopper; a weighed portion was removed and tumbled end over end with an appropriate solvent. The extracted mass was poured into a large beaker and sufficient anhydrous sodium sulfate added, with stirring, to separate the liquid phase. This liquid was filtered through additional sodium sulfate.

Aldrin was extracted with n-hexane and determined by the method of O'Donnell et al. (11).[2/]

Heptachlor was extracted with either n-hexane or a 2:1 mixture of n-hexane and isopropyl alcohol and determined by the method of Ordas et al. (12).

Malathion was extracted with carbon tetrachloride and determined by the method of Norris et al. (10).

Diazinon and Phorate

The frozen tomatoes were chopped in a mechanical food chopper, a weighed portion was removed, the chopper cleaned, and the weighed portion returned to the chopper and rechopped with sufficient anhydrous sodium sulfate to produce a crumbly mass. This mass was tumbled end over end with an appropriate organic solvent for 30 minutes and the solvent phase filtered through additional sodium sulfate.

Diazinon was extracted with 30°-60° C. petroleum ether and the residue determined by the sulfide procedure of Gigger (8).

After extraction of the phorate with chloroform, it was determined by three methods in different years. The cholinesterase procedure of Giang and Hall (5), as modified by Hensel et al.[3/], was used, as well as the colorimetric procedure of Giang and Schechter (6) and the colorimetric total phosphorus procedure of Gigger (7), as modified by George (4). In the colorimetric procedure for determining phorate residues, the solvent extract was oxidized with perbenzoic acid before chromatographing. A few of the phorate samples were extracted by other procedures used in the following section.

Di-Syston, Dimethoate, Guthion, and Mevinphos

The frozen tomatoes were ground in a mechanical food chopper and a weighed portion was blended for 2 to 3 minutes with an appropriate organic solvent. The blended sample was poured into a large beaker and sufficient anhydrous sodium sulfate added, with stirring, to separate the phases. The sample was allowed to stand for 10 minutes and the solvent phase filtered through additional sodium sulfate.

2/ Numbers in parentheses after the authors' names refer to Literature Cited at the end of this report.

3/ Hensel, Jack, Hewitt, A. E., Sheets, U. M., and Scott, R. C. Microestimation of demeton residues. Paper presented at meeting of Amer. Chem. Soc., Kansas City, Mo., 1954. [Unpublished. Title in Abstract of Papers.]

Di-Syston residues were extracted with chloroform. A part of the chloroform extract was evaporated to dryness with a gentle stream of air in a water bath. Three ml. of chloroform was added to dissolve the residue, and 1 ml. of 0.05-percent perbenzoic acid solution in a 1:10 mixture of benzene and chloroform and 1 ml. of 0.02-percent malachite green hydrochloride in chloroform were added. The sample was placed in a water bath at 50° C., removed at the end of 1 hour, cooled to room temperature, and read in 1-ml. cuvettes at 570 mμ. Standards were prepared in the same manner.

When the colorimetric method of analysis for dimethoate of George et al.[4/] was used, dichloromethane was used as the solvent. A weighed portion of the chopped frozen tomatoes was blended with dichloromethane and solid sodium chloride, the sample centrifuged, and the solvent phase filtered through anhydrous sodium sulfate. Chloroform extracts were analyzed by the total phosphorus method of Gigger (7), as modified by George (4).

Guthion samples were extracted with chloroform and analyzed by the method of Averell and Norris (1), as modified by Meagher et al. (9).

The cholinesterase procedure of Giang and Hall (5), as modified by Hensel et al.,[5/] was used to analyze the chloroform extracts of mevinphos residues.

Naled and Trichlorfon

Where naled was to be determined, 100 g. of chopped frozen tomatoes was blended with 4 ml. of concentrated hydrochloric acid in 50 ml. of water and the blended material was tumbled with 400 ml. of petroleum ether. The sample was poured into a large beaker, additional sodium sulfate added, and the solvent phase filtered through sodium sulfate, as described by the California Spray Corporation (2). Naled was determined by the cholinesterase procedure of Giang and Hall (5), as modified by Hensel et al.[6/]

Trichlorfon samples were extracted by blending the chopped tomatoes with 50 to 75 ml. of distilled water and removing the solid phase by filtration. The cholinesterase activity of the water extracts of the trichlorfon samples was determined by the method of the Chemagro Corporation (3).

CLEANUP PROCEDURES

It was found, by laboratory investigation, that cleanup of the solvent extracts of tomatoes was not required for all analytical procedures. Where a cleanup procedure was required, the following steps were taken:

4/ George, D. A., Walker, K. C., Giang, P. A., and Murphy, R. T. Colorimetric method for the determination of dimethoate residues. Paper presented at meeting of Amer. Chem. Soc., Atlantic City, N.J., 1962. [Unpublished. Title in Abstract of Papers.]

5/ See footnote 3.

6/ See footnote 3.

Phorate-Colorimetric Analysis

The phorate sample was oxidized with perbenzoic acid before being subjected to the cleanup procedure. The oxidized sample was chromatographed through a wet slurry (chloroform) column, as recommended by Giang and Schechter (6). Two ml. of 0.1 N sodium hydroxide was used in place of the suggested 3 ml. of 0.5 N sodium hydroxide.

Di-Syston-Colorimetric Analysis

A portion of the Di-Syston solvent extract was carefully evaporated to dryness, dissolved in 10 ml. of chloroform, and chromatographed through a chloroform-prewashed column of equal amounts of Columbia® activated charcoal and alumina. The Di-Syston was eluted with chloroform; the eluate was concentrated to 5 ml., shaken with 200-mesh Florisil®, filtered, and carefully evaporated to dryness.

Dimethoate-Total Phosphorus Analysis

A portion of the dimethoate extract was shaken with Nuchar C-190-N® and anhydrous sodium sulfate, filtered, the filter washed with chloroform, and the sample carefully reduced to a small volume. The partially cleaned up extract was chromatographed through a mixture of equal amounts of alumina:Nuchar C-190-N:MgO-Hyflo Super Cel®:60-mesh Florisil. The column was carefully eluted with chloroform and the eluate carefully evaporated to dryness.

Guthion-Colorimetric Analysis

A portion of the Guthion extract was concentrated to 25 ml. and chromatographed through a mixture of Attaclay®:Nuchar C-190-N:alumina. The column was eluted with a 1:1 mixture of benzene and chloroform.

RECOVERY OF KNOWN AMOUNTS OF INSECTICIDES

Known amounts of the different insecticides were added to nontreated control samples prior to extraction and the percentage recovery was determined. Companion nontreated control samples were analyzed and the recovery samples corrected accordingly. The values obtained are given in table 1.

DISCUSSION AND RESULTS

In table 2 is given the amount of insecticide residue on or in tomatoes resulting from various treatments.

Several types of insecticide treatments were used. Granules, dusts, and sprays were applied to the foliage. Sometimes the sprays had molasses, sugarbeet juice, or beet sugar added so that the insecticide would be held on the foliage for a longer time. Baits made of clay, molasses, vinegar, yeast, and an insecticide were put on the ground around the plant within a few days of harvest to trap fruit flies. Soil treatments consisted of granules applied topically either to the seedbed or to the soil when the plant was transplanted. Starter solutions containing nutrients and insecticide were poured into the hole before transplanting the tomato plant. Pelletized seeds were

made from seed, clay, and insecticide. The small pellets helped to retain moisture around the germinating seed.

Guthion at 0.75 pound per acre in three spray applications 0 and 3 days after treatment left measurable residues on the fruit at harvesttime, as did malathion as a bait at 0.27 pound per acre 4 days after treatment. The amount of residue found on the Guthion- and malathion-treated tomatoes was well below the established tolerances for these compounds (see p. 2). The malathion residues from treatment at 0.27 pound per acre may have been due to contamination of the fruit during the baiting process. With bait at 2 pounds of actual malathion per acre, no measurable residues were found on the mature fruit 4 days after treatment.

Where malathion dust was applied at 1.75 pounds per acre, the residues 4 days after application averaged 0.32 p.p.m. Eight days after application the residues were below the lower limit of accuracy of the analytical method as employed. This lower limit will vary depending on the method used (colorimetric, gas chromatography, cholinesterase), the size of the sample actually analyzed, and the efficiency of the cleanup procedure.

When 3 pounds of actual trichlorfon per acre was applied as granules to the foliage, the average residue 1 day after application was 0.08 p.p.m., or equal to the lower limit of accuracy of the analytical method. On this particular set of samples the residues ranged from less than 0.08 to 0.11 p.p.m.

With the exception of the samples cited, no measurable residues were found. For the phorate samples, various analytical procedures were used in different years (e.g., total phosphorus, colorimetric, cholinesterase) and different lower limits were attainable. The difference in lower limits explains the difference in the values reported in table 2 (e.g., <0.04, <0.06, <0.20 p.p.m.).

SUMMARY

Tomatoes were treated with two chlorinated hydrocarbon and nine organic phosphorus insecticides. Treatments ranged from seed treatment before planting to bait and foliage treatments on the day of harvest. Of the materials tested, only Guthion at 0.75 pound per acre in three spray applications 0 and 3 days after treatment produced measurable residues and malathion as a bait at 0.27 pound and as a dust at 1.75 pounds per acre 4 days after application. The residues found were well below the established tolerances for these two compounds.

Three pounds of trichlorfon applied as granules to the foliage left an average residue 1 day after treatment of 0.08 p.p.m. This value was equal to the lower limit of measurement of the analytical method.

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Table 1.-Fortification level and amount of insecticide recovered from fortified control samples

Insecticide	Fortification level	Insecticide recovery		
		Low	High	Average
	(P.p.m.)	Percent	Percent	Percent
Aldrin----------	0.40	86	97	90.0
Diazinon--------	.20-2.0	61	120	82.7
Dimethoate------	.20-1.0	68	117	79.0
Di-Syston-------	.25- .50	73	76	74.4
Guthion---------	.10- .50	90	120	106.2
Heptachlor------	.03- .59	69	122	98.1
Malathion-------	1.2 -1.7	71	114	94.8
Mevinphos-------	.02- .60	59	87	76.9
Naled-----------	.15- .25	64	117	76.9
Phorate---------	.30-2.0	67	120	86.6
Trichlorfon-----	.03- .20	69	107	88.0

Table 2.-Amount of insecticide residue on or in tomatoes resulting from various treatments

Insecticide treatment (pounds per acre)	Days between last treatment and sampling	Amount of residue	
		Range[1/]	Average[2/]
	Number	P.p.m.	P.p.m.
Aldrin bait, 0.0002----------	2	---	<0.05
Diazinon:			
Bait:			
0.0002----------	2	---	< .15
.135----------	4	---	< .15
1.0----------	0	---	< .15
Dust, 1.0----------	4	---	< .15
	8	---	< .15
Granules to foliage:			
1.0----------	0	---	[3/] <.15
	1	---	[3/] <.15
	3	---	[3/] <.15
1.5----------	2	---	<.15
Spray, 0.75----------	0	---	<.15
	1	---	<.15

Table 2.-Continued

Insecticide treatment (pounds per acre)	Days between last treatment and sampling	Amount of residue	
		Range[1]	Average[2]
	Number	P.p.m.	P.p.m.
Dimethoate spray (5 applications), 0.75	41	---	<.10
	68	---	<.10
	84	---	<.10
Di-Syston starter solution, 0.50	92	---	<.05
Guthion spray (3 applications), 0.75	0	<.10-.26	.23
	3	<.10-.24	.12
	7	<.10-.12	<.10
	14	---	<.10
	21	---	<.10
Heptachlor:			
Bait:			
0.0002	2	---	<.10
1.0	0	<.10-.12	<.10
Granules to foliage, 3.0	2	---	<.10
Malathion:			
Bait:			
0.0002	2	---	<.20
.27	4	---	[3] .21
2.0	0	---	<.20
Dust:			
1.75	4	---	.32
2.5	8	---	<.20
	4	---	<.20
Granules to foliage:			
3.0	0	---	<.20
4.8	2	---	<.20
Mevinphos:			
Phorate granules to seedbed, 2.0, plus mevinphos spray (foliage), 1.0	155	---	[4] <.06
Dimethoate in starter solution, 0.75, plus mevinphos spray (foliage), 1.0	103	---	[4] <.06
Spray (5 applications), 0.75	41	---	<.005
	68	---	<.005
	84	---	<.005

Table 2.-Continued

Insecticide treatment (pounds per acre)	Days between last treatment and sampling	Amount of residue	
		Range[1]	Average[2]
	Number	P.p.m.	P.p.m.
Naled:			
Granules to foliage:			
2.0	0	---	<.005
	1	---	<.005
3.0	1	---	<.005
Spray (5 applications), 0.75	41	<.005-.008	<.005
	68	<.01 -.016	<.01
	84	<.01 -.013	<.01
Phorate:			
Granules to soil, 1.0	84	---	<.20
Granules to seedbed, 1.75	156	---	<.20
Granules to seedbed, 1.75, plus spray (foliage) with 7 percent of molasses, 0.50	85	---	[3]<.20
	114	---	<.20
Seed, pelletized, 0.0625	200	---	<.06
Starter solution:			
0.25	77	---	<.04
	84	---	<.04
.50	77	---	<.04
	84	---	<.04
Starter solution, 0.25, plus spray (foliage), 1.0	0	---	<.04
Starter solution, 0.50, plus spray (foliage), 1.0	0	---	<.04
	7	---	<.04
Starter solution, 0.50, plus spray (foliage) with 7 percent of molasses, 1.0	85	---	<.20
Dimethoate in starter solution, 1.0, plus topical phorate granules, 4.0	103	---	[4]<.06

Table 2.-Continued

Insecticide treatment (pounds per acre)	Days between last treatment and sampling	Amount of residue	
		Range[1]	Average[2]
	Number	P.p.m.	P.p.m.
Spray (foliage):			
1.0----------	0	---	<.04
With 7 percent of molasses,0.50--	85	---	<.20
With 12 percent of sugarbeet juice (2 applications), 0.50----------	97	---	[3]<.20
5 applications, 0.35----------	41	---	<.20
	68	---	<.20
	84	---	<.20
With 10 percent of sugarbeet juice (5 applications), 0.35---------	41	<.20-.20	<.20
	68	---	<.20
	84	---	<.20
With 10 percent of beet sugar,0.35	41	<.20-.30	<.20
	68	<.20-.20	<.20
	84	---	<.20
Trichlorfon granules to foliage:			
2.0----------	0	---	<.02
	1	<.02-.02	<.02
3.0----------	1	<.08-.11	.08

1/ Range is shown for those samples where one or more individual samples exceeded the lower limit of accuracy of the analytical method employed.

2/ These data have been corrected for the appropriate control samples, but not for the average recovery.

3/ These samples were washed.

4/ Run by a total phosphorus method that would determine both insecticides, but calculated as the last insecticide used.

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If you use insecticides, apply them only when needed and handle them with care. Follow the directions and heed all precautions on the container label. If insecticides are handled or applied improperly, or if unused portions are disposed of improperly, they may be injurious to humans, domestic animals, desirable plants, honey bees and other pollinating insects, fish, and wildlife, and may contaminate water supplies.